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Quantum coherence in photosynthesis

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Abstract

Quantum coherence improves the quantum efficiency of excitonic energy transport within the Fenna-Matthews-Olson photosynthetic complex from the green sulphur bacterium, *Chlorobium tepidum*. Experimental evidence from third-order nonlinear spectroscopies provides clear evidence of quantum coherence among excited states persisting for picoseconds despite rapid (<100fs) dephasing of quantum coherence between ground and excited states. This protection of quantum coherence can arise from multiple mechanisms, but the net effect is the same: the energetic landscape is course-grained thereby improving efficiency by effectively smoothing the rugged energetic landscape while simultaneously eliminating trap states. The protein bath enables the unusual observed dynamics and illustrates some simple design principles that provide direction to synthetic efforts to mimic the effect. This communication provides an overview of experimental and theoretical notions for those interested in exploiting design principles of photosynthetic energy transfer in synthetic systems.

Keywords: Quantum Biology, Ultrafast Spectroscopy, Photosynthesis

1. Introduction to Quantum Biology

Evolution is the ultimate opportunist. Traits will persist whenever they convey improved fitness. There is nothing more to it. Biology does not select based on whether a mechanism can be modeled classically or quantum mechanically – only if it works. There is no reason to believe that all biology must exist in the correspondence limit where the underlying quantum effects can be captured by classical models. Similarly, there is no reason to expect manifestly quantum effects in biology unless they provide some competitive advantage.

Quantum biology involves the search for (and subsequent study of) these manifestly quantum effects in biological systems. Except for some rather unusual and exciting experimental methods to probe consequences of phase, coherence, and entanglement, this field hardly differs from other areas of biophysics. In my opinion, a central goal of quantum biology must be to elucidate new design principles underlying biological systems and to demonstrate this understanding by applying these ideas to synthetic system. This is not merely an academic endeavor – new design principles will likely spawn new devices and technology as well as an improved understanding of basic science.

Quantum effects in biology have been posited in olfaction, magnetic sensing, photosynthetic energy transfer, photoenzymology, molecular motors, ion channels and even consciousness [1–6]. It is my hope that experimental endeavors to verify these hypotheses will uncover new and broadly applicable design principles. At the same time, some

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of these suggestions may be proved false. Time will tell. Even if proven false, these hypotheses may prove valuable if the underlying principle can be applied regardless of whether biology exploits it. Similarly, design principles from biological systems might be applied broadly as our desires may well differ from the specific applications that convey evolutionary fitness. In this manuscript, I will focus only on photosynthetic energy transfer, but I challenge the reader to explore new ideas and to propose new experiments for all quantum effects in biology.

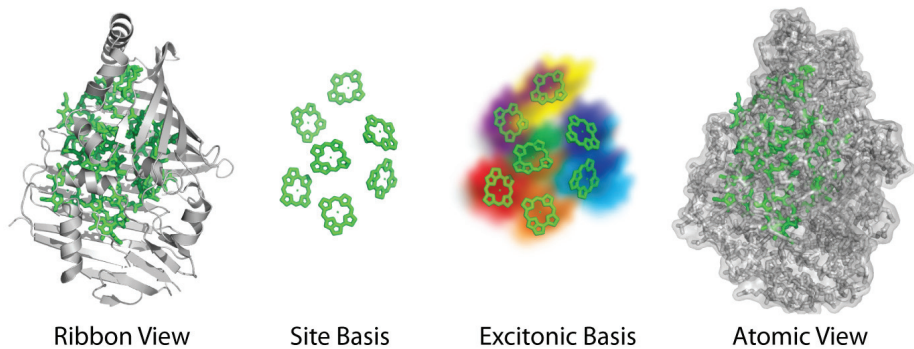

Figure 1: The Fenna-Matthews-Olson protein-pigment complex from the green sulphur bacteria *Chlorobium tepidum* consists of 8 bacteriochlorophyll molecules (green) surrounded by a protein [7]. This complex conducts energy from a large antenna to the reaction center and yielded the first data demonstrating wavelike energy transfer [3, 8]. Four visualizations of the complex are shown: the protein represented as a ribbon, the bare chlorin rings that contain the transition dipoles probed by a laser (i.e. the site basis), the excitonic basis with the singly excited states shown as density clouds, and an atomic view showing how crowded the environment surrounding the chromophores actually is.

2. Photosynthetic Energy Transfer

Fundamentally, sunlight is a diffuse resource and the reaction centers, which serve as the basic photosynthetic engine, simply cannot collect enough light on their own. Over the past two and a half billion years, photosynthetic organisms have evolved antenna systems to harvest solar light with nearly perfect quantum efficiency. These photosynthetic antennae are metabolically inexpensive and permit the reaction centers (which are more expensive, often involving iron and/or manganese) to operate at peak efficiency despite their relatively small absorption cross-section [9]. For example, a reaction center under typical conditions might be able to turn over biochemically 300 times per second but can only collect three photons per second. Rather than creating a hundred reaction centers, an organism can just as well create an antenna that increases the absorption cross-section of a single reaction center. In this regard, photosynthetic systems employ a division of labor between light-harvesting (absorption) in the antennae and charge separation in the reaction center.

The energy transfer process within photosynthetic antennae demonstrates remarkable quantum efficiency. To model this energy transfer process, the traditional approach has been to consider dipolar couplings and use Förster resonance energy transfer (FRET) amidst an incoherent bath [10]. By invoking the secular approximation, which eliminates coherence transfer, this model yields simple exponential dynamics, which can fit the observed population transfer rates with appropriate assumptions. To understand the extreme quantum efficiency using this model, relatively strong couplings are needed to permit fast transport to the reaction center and coupling to trap states must be avoided. For most bacterial complexes, this model provides an excellent qualitative fit. In the model and in practice, the excitation can hop downhill toward the reaction center dissipating some energy at every step. Plants are different. The major distinction between these two systems is that in bacterial antennae, the bluest chromophores tend to be farthest from the reaction center while in plants no organization is immediately obvious or apparent [11]. I note that the organization of chromophores, however, is highly conserved; thus, while no simple organizational principle is easily observed, such a principle likely exists. For plant systems, the kinetic models based on FRET offered little guidance on how traps can be avoided.

Accurately visualizing the energy moving through the photosynthetic complex presents a challenge. Typical ribbon representations of the protein as shown in Figure 1 highlight the protein backbone, yet the lasers used to

interrogate the energy transfer process only probe the chromophores. While thinking of each chromophore separately is tempting, we must remember that the chlorophylls couple to each other. (This coupling is the essence of how nature uses a single compound, chlorophyll, for a myriad of tasks.) The best way to think about the complex is to visualize the excited states (called excitons) as delocalized across multiple chlorophyll molecules. This excitonic basis maps easily onto frequency resolved spectroscopy while maintaining some spatial locality. This excitonic basis also provides a natural connection to the Hamiltonian which governs time dependence. The reader is warned however not to disregard the protein entirely; it surrounds the excitons and provides the solvating bath that will govern relaxation. Without the bath, the system would be time-independent and could not function! The bath dictates all dissipative energy transport, both coherent and incoherent.

When long-lived quantum coherence was first observed in photosynthetic complexes in 2007, coherence transfer could no longer be ignored [3]. The wavelike energy transfer implied by this coherence surviving beyond population lifetimes required a fundamental change in how we model photosynthetic pigment-protein complexes. At the heart of the FRET model was an incoherent bath assumption, but this approximation effectively forbids the observed oscillatory dynamics. The observation of long-lived coherence (taken to imply coherence transfer) immediately led to models from quantum information theory where interferences among coherences provide a mechanism to exceed classical limitations [12, 13]. The leading models developed simultaneously by Aspuru-Guzik and coworkers and Plenio and Huelga show an interesting feature: some dephasing enhances transport that might otherwise be quashed by disorder, but if too rapid, dephasing can limit transport [12, 13]. The notion that a middle ground between purely coherent and purely incoherent transport can outperform either extreme offers insights for how to design novel systems for solar light harvesting, detection and simple information processing [12]. In this manuscript, I seek to explain the experimental observation of quantum coherence in photosynthetic systems as well as the theoretical constructs and ideas used to explain it.

3. Quantum coherence

Unlike classical systems which can be fully described by simultaneous measurements of observable quantities such as position, momentum or energy, quantum systems must be described by wavefunctions (or a density matrices, more generally) [14]. From this wavefunction, which is generally time dependent, the expected value of any observable can be calculated. However, an experimentalist probing such a quantum system may never observe this expected value. Rather, each experimental observation of a single quantum system will yield an eigenvalue, a_i, of the associated operator $\hat{A}$. Only on average will the expected value be obtained. States of quantum systems without sharp observables are said to be superposition states in the eigenbasis of the relevant operator. Such states are the norm rather than the exception because many operators do not commute. That is, the state of the system,Ψ, is described by a superposition of eigenfunctions, ϕ_i:

$$\Psi = \sum_i c_i \phi_i \text{ such that } \hat{A}\phi_i = a_i \phi_i. \tag{1}$$

For a large ensemble, this distinction may not seem important because any observable quantity corresponding to some operator, $\hat{A}$ will necessarily be averaged over the observed ensemble:

$$\left\langle \hat{A} \right\rangle = \sum_i |c_i|^2 a_i. \tag{2}$$

However, we need to be able to distinguish between two apparently similar situations: an ensemble of superpositions and an ensemble containing a mixture of systems in different eigenstates [15]. These two situations are fundamentally different, yet both ensembles would show the same (initial) expectation value for the observable. For example, consider a two state system consisting of a ground and excited state, $|g\rangle$ and $|e\rangle$ respectively, such that the two states are time independent eigenfunctions of the Hamiltonian with different energies. In an ensemble consisting of a mixture between excited and ground state components, no observable will be time dependent because every element of the ensemble is in a time independent state. In contrast, an ensemble consisting of even superposition states will be time dependent. That is, the wavefunction for each member of the homogeneous ensemble is given by

$$\Psi(t) = \frac{1}{\sqrt{2}} e^{\frac{-iE_g t}{\hbar}} |g\rangle + \frac{1}{\sqrt{2}} e^{\frac{-iE_e t}{\hbar}} |e\rangle . \tag{3}$$

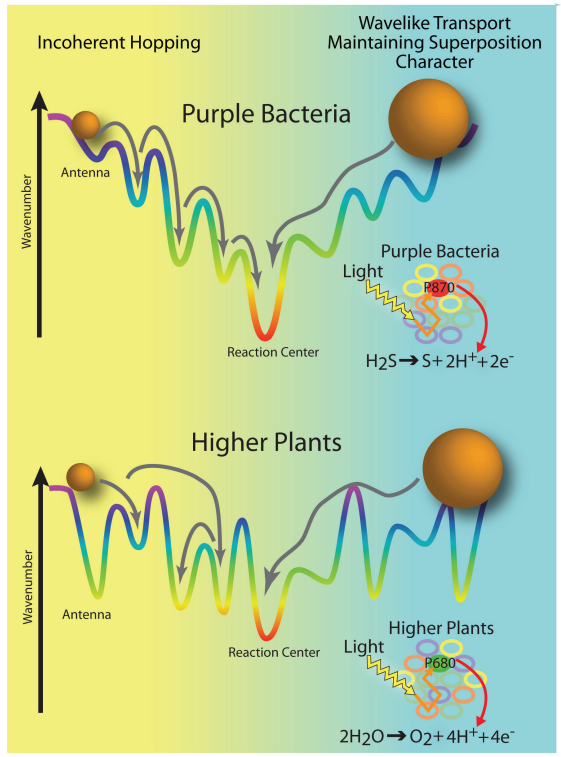

Figure 2: The energetic landscape in commonly studied bacterial light harvesting tends to have a simple dissipative organization with chromophores nearer the reaction center having lower transition energies. As such, incoherent hopping provides a reasonable mechanism for navigating this landscape while coherent transport simplifies the process by simply course-graining the landscape. For higher plants, the landscape is rugged and not obviously "tilted" toward the reaction center. Coherent transport is likely to be much more important in such an environment.

Each Hamiltonian eigenstate contributing of this superposition state evolves phase at a different rate. For operators that do not commute with the Hamiltonian, such as the dipole operator responsible for optical spectroscopic signals, observables will oscillate in time with frequency, $\omega_{eg} = \left(E_e - E_g\right)/\hbar$. This phase is a unique feature of quantum mechanics that follows directly from the time dependent Schödinger equation [15].

To distinguish between the two situations described above, the density operator, $\hat{\rho} = |\Psi\rangle\langle\Psi|$ is used. In the matrix representation of the density operator, the diagonal elements of the operator corresponding to the superposition of ϕ_i states will have the form $\rho_{ii} = |c_i|^2$. These elements represent the likelihood of observing the eigenvalue a_i. In the specific two-state case above, both diagonal elements are $\frac{1}{2}$. For an even mixture of systems in either the ground or excited state, the diagonal elements would also be $\frac{1}{2}$. These diagonal elements are called populations and correspond to the likelihood of observing a given state but contain no information about why the state would be observed. Are some elements of the ensemble simply in this state? Are the elements of the ensemble in a superposition to which this state contributes? Populations simply cannot distinguish between mixed states (mixtures) and pure states (representable by a single wavefunction) arising from superpositions, to say nothing of the vast space between these two extreme situations.

The off-diagonal elements of the density matrix are called coherences, and they contain information regarding the superposition states within the ensemble. In particular, they express the magnitude of the phase evident in the system. For the pure superposition state in equation 1, these elements have the form $\rho_{ij} = c_j^* c_i$ [15]. Interestingly, it is the average phase within the ensemble that matters. That is, a mixture of superpositions with arbitrary phase has the same density matrix and time evolution as a mixture of eigenstates.

The case of a single molecule ensemble is especially interesting to consider because in this context a mixture takes on a different meaning that is best described within the context of quantum information theory. A pure superposition

state with a known wavefunction (and therefore maximum possible information) and phase will necessarily yield a density matrix with coherences. In contrast, a mixed state (previously described as a 'mixture" but that nomenclature becomes muddled for a single molecule ensemble) represented by a density matrix with all off-diagonal elements equal to zero simply reflects the lack of information regarding the state of the system.

From the discussion above, it is clear that coherences and populations are basis set dependent quantities. Because the time dependent Schrödinger equation involves the Hamiltonian operator, the time dependent behavior of populations and coherences in the eigenbasis of the Hamiltonian is worth considering explicitly. In this basis set, populations do not evolve phase, while coherences do evolve phase as the Hamiltonian operator operates on each element of the density matrix from both the right and the left. For this reason, I will only express density matrices in the basis set of the Hamiltonian for the rest of this work. Of course, changing basis set will never change observable photophysics but can increase the apparent complexity of the dynamics.

4. How to think about quantum coherence?

Treating a molecular spectroscopy experiment semiclassically, the oscillating electric field from a short laser pulse couples Hamiltonian eigenstates to one another through the dipole operator necessarily leaving the system in a superposition of Hamiltonian eigenstates [16]. If excited with coherent light, the entire ensemble will be left in a coherent state as the electron cloud surrounding each molecule continues to resonate or "ring" in phase with the optical field.

Ultimately, the coherence will dephase because of small differences within the ensemble, which to this point we have considered to be homogeneous in the strictest sense (perhaps absurdly so). For example, when the energy gaps between different elements of the ensemble differ, each element of the ensemble will evolve phase at a slightly different rate and the ensemble will eventually dephase [17]. The off-diagonal elements will tend to zero, and the populations will persist. It is important to note that this simple interpretation is only true in the Hamiltonian eigenbasis where the population elements will ultimately reach thermal equilibrium ($\rho_{ii} = e^{-E_i/kT}$ and $\rho_{ij} = 0$ where $j \neq i$) [15].

Coherence, therefore is a relatively fleeting quantity. In photosynthetic complexes, the coherence between ground and excited states that is excited by the optical field persists for only 70fs at 77K (liquid nitrogen) and about 20fs at room temperature [18]. These coherences therefore dephase before even the fastest energy transfer timescales (about 150-300 fs) become relevant. However, coherences between excited states apparently persist much longer based on experimental observations. Such coherences are created by any fast excitation process, which by definition will not commute with the Hamiltonian and will generally couple the ground state to multiple excited states. Ultrafast laser pulses have this property, but so will other forms of excitations such as spatially localized "hopping" processes.

Before the coherence among excited states dephases, the excitation maintains a superposition character and does not yet behave like a simple mixture of excited states. While not a formal definition of coherence, this notion of superposition character provides a simple interpretation for the observable effects resulting from quantum coherence. In particular, quantum beating in observables that do not commute with the Hamiltonian is a direct consequence of this superposition character. Perhaps less obvious, yet equally enlightening is the effect of quantum interference. Whenever the ensemble maintains some average phase, interference – either constructive or destructive – must be considered. For example, destructive interference in a coherent system might disallow transfer to a trap state or constructive interference might enhance transport to the target state. This effect arises because probabilities in quantum mechanics come from the square of the sums of the amplitudes as compared to incoherent (classical) mechanisms which give probabilities based on the sum of the squares of amplitudes [13].

The net phase within the ensemble provides new opportunities for chemical reactivity even without complete fidelity. For example, destructive interference need not lower a rate constant to zero; simply depressing the rate constant is enough to affect chemical dynamics. Similarly, enhancement based on constructive interference can behave in the same manner. Therefore, opportunities exist to exploit long-lived quantum coherence to adjust rate constants without adjusting the couplings. Interference provides another route to manipulating rates that does not appear in simple incoherent models such as Fermi's Golden Rule calculations that provide the foundation for most chemists' intuition.

5. Evidence of quantum coherence from quantum beating signatures

Quantum beating in spectroscopic measurements provides a direct measure of quantum coherence and dephasing on the appropriate energy and time scales. To date, the most common spectroscopy used to explore quantum beating among electronic states (as compared to vibrational quantum beating) has been two dimensional electronic spectroscopy [3, 18–22]. A detailed and excellent introduction to two dimensional electronic spectroscopy has been created by Fleming and coworkers [17]. I will not try to duplicate that work here, but rather describe specific analogies and aspects of the technique that make it ideally suited for interrogating quantum coherence and wavelike dynamics. One such benefit of two dimensional spectroscopy is that energy transfer (between states of different energy) appears off the main diagonal permitting improved resolution in congested electronic spectra. Of course, spectral congestion is not necessary nor even desirable, but in practice, close lying states separated spatially rather than spectrally provide efficient energetic transport (but also congested spectra). This is precisely the strategy evident in photosynthetic complexes that have provided the impetus for the current discussion. Further, quantum beating involves phase evolution and two dimensional spectroscopy is a phase-resolved technique though we will see that this feature is not strictly necessary.

Two dimensional electronic spectroscopy is the optical analog to two dimensional NMR and uses a stimulated echo pulse sequence borrowed directly from the NMR COSY sequence [23, 24]. The dominant dipolar couplings that result in the electronic energy transfer also cause this spectroscopy to bear many important resemblances to the NMR NOESY technique at longer delay times. Despite the apt analogies to NMR, optical spectroscopy is complicated by a number of factors: 1) no clear separation of timescales results in dynamic line broadening due to disappearance of inhomogeneity (that is no clear T_1 or T_2 definitions), 2) pulses very near the weak coupling limit ($\pi/100000$) complicates use of the Bloch sphere model, 3) generation of optical pulses with prescribed phase is not possible which complicates phase cycling, 4) timescales faster than available electronics necessitates optical gating. Nonlinear optical spectroscopy has only one advantage over NMR, and it is important: the sample is large compared to the optical wavelength so signals are emitted in specific and unique directions due to conservation of linear momentum of the photons. Exploiting this directional signal enables "phase-matching" simply by observing only the signal beam emanating in the proper direction. This strategy provides as a very simple alternative to phase-cycling.

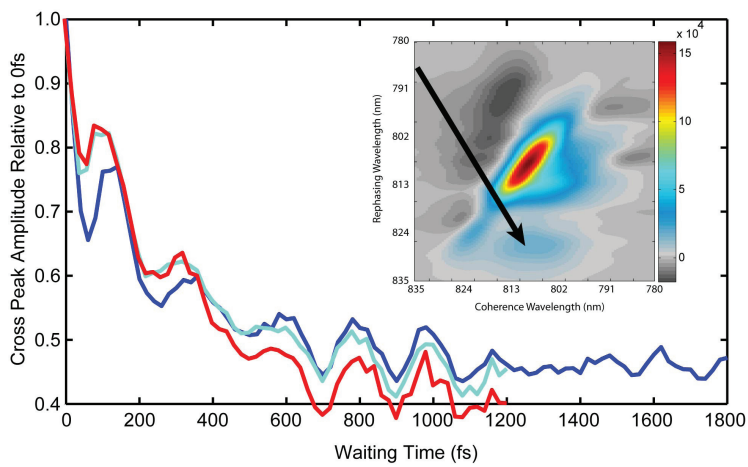

Figure 3: Quantum beating indicating long-lived coherence. Two dimensional spectra of the Fenna-Matthews-Olson complex show clear beating signals in the cross-peak between excitons 1 and 2 as a function of waiting time. The three beating traces represent three replicates prepared and sampled independently. The agreement in phase and frequency indicates that this beating is not an experimental artifact.

In two dimensional optical spectroscopy, the signal arises from interference (or lack thereof) between response pathways represented by different double-sided Feynman diagrams [25–27]. An example of a double sided Feynman diagram representing a rephasing pathway responsible for a quantum beating signal is shown in Figure 4. Each diagram represents a term of the perturbative expansion, and phase-matching permits selective isolation of a small number of these terms. Yet, individual pathways cannot be isolated.

No spectral feature can, therefore, be assigned to any single diagram complicating interpretation of the spectra [15]. This aspect, however, can be useful for identifying oscillatory phase components within the spectrum. For example, dynamic features originating from the sum of a static pathway (no phase evolution) and a pathway with oscillating phase will give rise to beating even without phase-resolution. That is, alternating constructive and destructive interference between the two pathways will yield a beating in the magnitude of the overall signal [28]. Without such interference, phase-resolution would be strictly necessary to detect such beatings. Optical spectroscopies can, of course, be phase-resolved. However, the optical pulses can not be generated with prescribed phase (a limitation of current optical field generation technologies). A "phasing" procedure must therefore be employed to recover the absolute phase thereby separating the real (absorptive) part of the signal from the imaginary (dispersive) part. This process presents many opportunities for errors that might well generate oscillatory artifacts. In contrast, magnitudes (the absolute values of the signal) provide an excellent check on the system to ensure that beating is not an artifact of improper phasing. Deciding which approach to use is not necessarily straightforward. The real part of phase-resolved data provides improved resolution by eliminating broad dispersive contributions to the response, but phase-rolls and improper phasing can create artifacts in the dataset. Generally, both approaches should be used to verify that the beating is real and to evaluate whether incorporating phasing errors is justified by the improved spectral resolution.

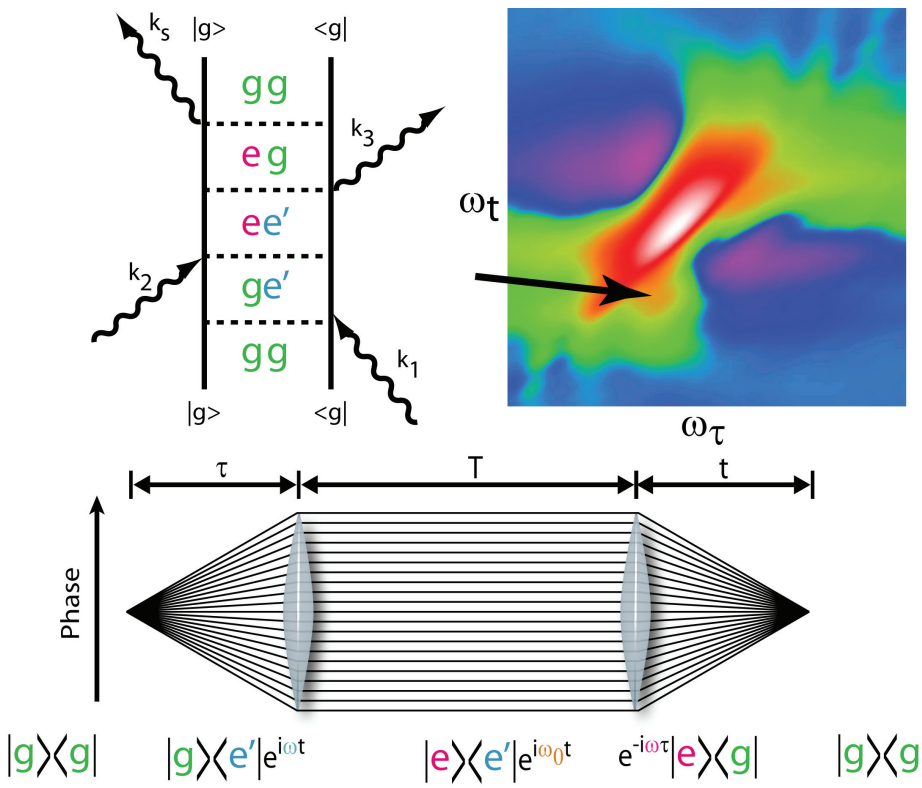

Figure 4: Two-dimensional electronic spectroscopy uses three pulses to interrogate the third-order nonlinear response. This response signal is described perturbatively using Feynman diagrams as shown in the upper left. After Fourier transforming over the first and third delay times, a two dimensional spectrum (upper right) is obtained. Analogous to a spin echo, the phase evolution can be plotted relative to the ensemble mean to obtain the "lens diagram" (center bottom). When the state during the second delay time or waiting time, T, involves two different excited states in the one exciton manifold, a slow quantum beating signal will appear in a series of two dimensional spectra. This beating signal reports on coherence among the excitonic states.

To measure the lifetime of quantum coherence against dephasing, an exponential decay representing pure dephasing multiplied by a sine wave provides a simple but effective model of the signal magnitude [18, 22]. The best resolved beating signals generally appear off the main diagonal in a two dimensional spectrum where incoherent energy trans-

fer pathways (which do not evolve phase) interfere with pathways that involve zero-quantum coherences, which report on superposition character among excited states. Locating these beating signals far from the main diagonal provides improved spectral resolution as well as a secondary check on the signal by comparing rephasing (echo) signals with non-rephasing (free-induction decay or "FID") signals that do not contain electronic beats [28]. The location of these signals also indicates why two-dimensional spectroscopy provides an ideal platform for detecting quantum beating signatures – other spectroscopies can not provide the necessary simultaneous frequency and temporal resolution.

6. Understanding the ramifications of wavelike transport

In classical incoherent transport models, coherences dephase quickly and populations display simple first order kinetics evidenced by dynamics described by exponential growths and decays. Never do the populations and coherences couple nor do coherences mix among themselves. In generalized quantum transport models, all elements of the density matrix can couple to all other elements and generally do, as illustrated by the Redfield equation of motion:

$$\frac{\partial \rho_{ij}}{dt} = i\left(\varepsilon_i - \varepsilon_j\right)\rho_{ij} - \sum_{kl} \kappa_{ij,kl}\rho_{kl} \tag{4}$$

where ε_i is the energy of the ith eigenstate of the Hamiltonian and $\kappa_{ij,kl}$ is the relaxation superoperator that permits coupling between all elements of the density operator.

Coupling among coherences permits wavelike transport, a manifestly quantum effect that is similar to coupled, radiating classical antennae. Such dynamics permit relaxation without loss of superposition character. The conditions of the density matrix require transfer of coherence or dephasing to accompany population transport. Within the secular approximation, coherence is destroyed with energy transfer because coherence transfer is ignored. Recent data showing long-lived coherences, however, indicates that this model is incomplete and that coherence transfer is important to understanding the robustness of photosynthetic energy transfer [12, 29].

Detailed models of this energy transfer process have been constructed and properly capture the effect of coherences transport. In this manuscript, I aim not to summarize these models but rather to provide analogies to help put these effects into context for a chemist attempting to engineer synthetic systems with similar excitonic transport properties.

First, let us consider the process in a time dependent manner. Fluctuations within the system-bath Hamiltonian mix the state of the system with phonons in the bath throughout the energy transfer process. Therefore, while we would very much like to think about a single, time independent Hamiltonian basis, *no such basis exists*. All the prior discussion actually refers to the "time-averaged" Hamiltonian; that is, the off-diagonal elements of the Hamiltonian are *on average* equal to zero for the excitonic basis, but at any given instant are not likely to equal zero. The net effect of this process is that states mix and relaxation occurs even on the femtosecond timescale. As trap states or other local minima mix with states that permit rapid relaxation to the target state (typically a reaction center or the next complex en route to the reaction center), traps can be avoided [30]. The key to avoiding traps is therefore dynamic disorder. This is a very different paradigm from typical designs for energy transfer where disorder is to be avoided. The difference is that static disorder creates traps while dynamic disorder helps to avoid them. This is not a new observation – Förster knew about this notion in 1946 when he considered spectral overlap to formulate his theory of energy transfer [31]. The reason that photosynthetic energy transfer is somewhat different is because the timescales of relaxation permit coherent effects to matter. Put differently, the line that divides static from dynamic is not well defined for molecular motions on the femtosecond timescale.

Another equivalent way to think about this process is in the basis set of the time-averaged Hamiltonian. In the presence of significant coherence, each member of the ensemble spans many states. These superposition states effectively "course-grain" the energetic landscape permitting the excitation to avoid narrow traps. In the same way a small marble cannot navigate a grassy slope without becoming stuck on each blade of grass while a larger soccer ball rolls right down the hill, these superposition states permit more rapid sampling of the energy landscape as illustrated in Figure 2. It is clear that dephasing must play a role in such a system – without dephasing the excitation would rattle around such an energetic landscape forever. In photosynthetic complexes, this problem is avoided because the reaction center enables rapid dephasing after charge separation (the desired outcome!). The charge separated state dephases extremely quickly due to the long range interactions of the charged particles thereby quenching the coherent trasport precisely when the excitation reaches the reaction center. From this description, one might assume that dephasing

within the antenna always has deleterious effects. It does not. In the presence of disorder, a coherent excitation will localize (Anderson localization) and transport will be inhibited. Thus, when dephasing is slow but not too slow, the transport properties will be optimized [12, 30, 32]. The optimization conditions emerging from theoretical treatments of this process must be explored and verified [30].

7. The role of the protein

Necessarily, all the spectroscopy focuses on the excitonic states; those are the only states directly accessible and addressable with femtosecond laser pulses. From an evolutionary standpoint, however, the action resides squarely in the structure of the protein environment. This distinction is important. The coupling to bath modes drives the excitonic dynamics. The bath modes are not purely incoherent, yet statistical models of the bath treat them precisely this way. We do not yet understand the microscopic design principles required to permit long-lived quantum coherence. Electronic states generally dephase in tens of femtoseconds. How does the protein create electronic coherences that last for hundreds of femtoseconds or picoseconds?

Two leading models exist in the literature for how such a protein might protect quantum coherence. First, in direct analogy to decoherence-free subspaces in quantum information theory, we can consider a spatially correlated bath. Such a bath permits long-lived quantum coherence among excited states (zero quantum coherences) but generates rapid dephasing of single quantum coherences (between ground and excited states) [19]. In this regard, the bath does not fight electronic dephasing directly, but rather preserves only a portion of the coherence – the coherence among excited states. Microscopically, all the excitons spectrally diffuse together, which can only come from environmental fluctuations that affect all the excitons in the same manner [19]. Spatially correlation on the order of the size of the photosynthetic complex would create precisely this effect. Dielectric fluctuations, which arise from a mean field treatment of local fluctuations, might have similar character. Atomistic simulations in conjunction with point mutations will be necessary to text this hypothesis. In the meantime, brute force experimental techniques can be brought to bear on the problem by considering cross-linking the protein or inserting isotopic labels within the complex (perhaps broadly or randomly).

Another compelling model emerging from both experiment and calculation involves considering coupling between populations and coherences [33]. Coherences are generally short-lived, but perhaps they will persist longer if coupled to long-lived populations. Populations do not develop oscillating phase under unitary evolution, but coherences do. In the presence of coupling, we would predict oscillatory population dynamics and long-lived coherence. While examining the source of long-lived coherences may be difficult, proving that population terms oscillate is experimentally tractable. New data showing this effect may shed light on the precise protein motions required to enable long lived coherence.

In either case, the process requires some portion of the bath to behave quantum mechanically and to couple coherently to the initial excitation. While at first an exotic idea, this type of coupling is common and necessary. A strong change in dipole from ground to excited state will necessarily drive oscillations within the polarizable protein environment. Just like ringing a tuning fork, coherent phonons will be launched from this excitation. These coherent motions can easily generate all the effects described above.

8. Opportunities to exploit quantum effects in synthetic systems

Fundamentally, discovery of wavelike energy transfer in photosynthetic systems essentially emphasizes the polymeric nature of the protein. That is, the proteinaceous solvation environment creates an ordered, multiply connected environment where individual chromophores are affected by fluctuations in a correlated manner. No evidence to date implies that wavelike energy transfer is a result of extreme evolutionary finesse that could not be recreated in synthetic systems, although that might be the case. Some evidence, such as coherent transfer in conjugated polymers or J-aggregates, indicates that synthetic systems may demonstrate similar energy transfer dynamics though no synthetic system has yet been specifically designed or optimized for this wavelike energy transfer mechanism. To develop systems optimized for wavelike energy transport will require control of the spatial positions and orientations of chromophores, which dictate the electronic couplings as well as the spectral bath of phonon modes surrounding the system. Applications for such materials may ultimately include optoelectronics, solar light harvesting, on-pixel processing, and excitonic devices.

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